Toner Ink Particle Morphology in Air-Sparged Hydrocyclone Flotation Deinking

J.K. Borchardt, J.H. Rask, J.D. Miller, and Q. Yu

ABSTRACT

A series of pulping and flotation deinking tests were performed using a pilot-scale air-sparged hydrocyclone (ASH) flotation cell and a toner ink printed furnish. Microscopy studies indicate ink particles in both the flotation accepts and rejects are relatively flat. Many of the ink particles appear to be brittle and easily broken into smaller fragments. In some cases, toner ink particle softening had occurred as indicated by partial fusion of ink particles. Despite this softening, environmental scanning electron microscope (ESEM) images suggest toner ink particles were not elongated by the high shear conditions associated with the air-sparged cyclone flotation cell.

KEYWORDS

Deinking, Flotation, Hydrocyclones, Pilot Plants, Toners.

INTRODUCTION

ASH flotation technology has been developed at the University of Utah over the past decade (1-5). This technology has been refined (6) and installed in at least one commercial mill deinking recovered office paper (7,8). The specific capacity of ASH flotation cells is more than 100 times that of other flotation equipment. Unlike other flotation cells, ASH flotation occurs in a centrifugal field. A primary reason for the microscopy portion of the present study was to determine if toner ink particle elongation occurred under the centrifugal flow, relatively high shear conditions of this flotation cell.

The specific goals of the present research were to use environmental scanning electron microscopy (ESEM) to answer the following questions:

1. What is the size and morphology of residual photocopier ink particles remaining after flotation deinking using ASH flotation cells and a proprietary emulsified oil deinking agent?

2. Is there any evidence of toner ink particle softening in the pulper and elongation in the high shear environment of the flotation cell?

3. How does this ink particle morphology compare to that produced by proprietary deinking agents used in Denver cell flotation deinking tests?

Air-Sparged Hydrocyclone Technology

The ASH flotation cell is depicted in Fig. 1. It consists of a right-vertical tube having a jacketed porous wall, a conventional cyclone header with a vortex finder, and a froth pedestal/underflow structure which is centered on the cyclone axis at the bottom of the porous tube.

The deinking agent is added to the pulp slurry before its introduction into the flotation cell. The deinking agent is designed to increase ink particle hydrophobicity.

The pulp slurry is fed tangentially through the cyclone header to develop a swirl flow inside the porous tube. Pressurized air passes through the jacketed fine porous tube wall and is sheared into

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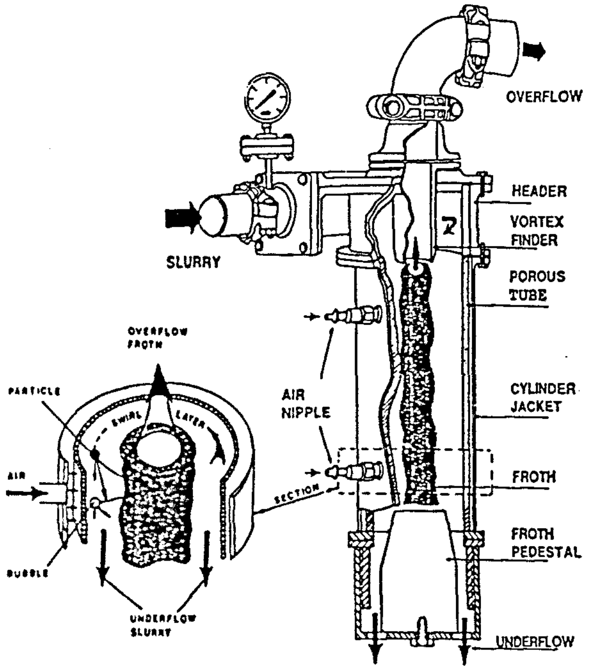
Borchardt is Staff Research Chemist, Shell Chemical Co., Westhollow Technical Ctr., P.O. Box 1380, Houston, TX 77251-1380, USA. Rask is Research Engineer, Shell Oil Co., Bellaire Technical Center, P. O. Box 481, Houston, TX 77025, USA. Miller is Professor, Dept. of Metallurgical Eng., Univ. of Utah, Salt Lake City, UT 84112, USA. At the time the article was written, Yu was Research Fellow, Dept. of Metallurgical Eng., Univ. of Utah, Salt Lake City, UT, USA. He is now with U.S. Gypsum, Inc., 700 N. Hwy. 45, Libertyville, IL 60048, USA.

FIGURE 1: **Schematic diagram of air-sparged hydrocyclone flotation cell.**



numerous small bubbles by the high-velocity swirl flow of the pulp slurry. Suspended ink particles in the pulp collide with these bubbles. After attachment of the hydrophobic ink particles to the air bubbles, the ink particles are transported radially into a froth phase which forms concentrically on the cylindrical axis. Thus flotation occurs in a centrifugal field. The froth is supported and constrained by the froth pedestal and this moves toward the vortex finder of the cyclone header. It is then discharged as a reject stream.

The cleaned fiber is discharged as an underflow stream through the annulus between the porous tube wall and the froth pedestal.

The pulp slurry input capacity is at least 200-400 gallons per minute per cubic foot of cell volume. Thus one 6-inch diameter x 50 inch length ASH cell (internal cell volume = 0.82 ft.^{3}) can process 250,000 gallons of pulp slurry per day. ASH flotation cell capacity is said to be 20-30 tons (dry paper basis) per day (8). (The external dimensions of the actual equipment with all parts mounted is about 8 inches in diameter x 80 inches in length.) The specific capacity of different flotation cells is compared in Table 1.

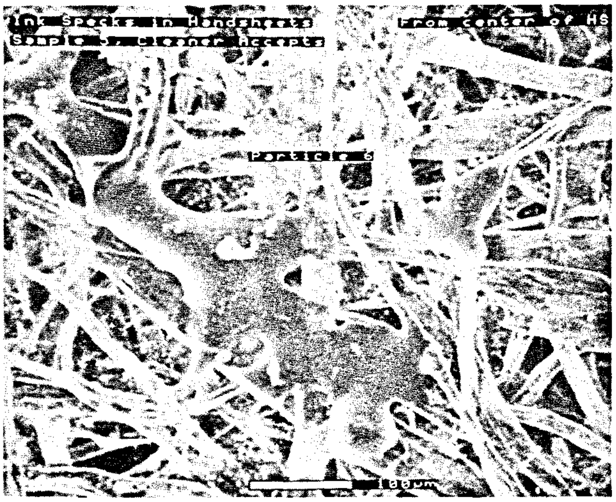
The specific capacity values cited in Table 1 are representative, not maximum, values. The residence time of the stock in the ASH flotation cell is on the order of seconds (8). The high shear environment of the ASH flotation cell is indicated by the high specific capacity of the ASH flotation cell relative to the other two types of flotation cell (Table 1). This high shear can reduce fiber entanglement. This promotes high ink separation efficiency. Studies suggest that fiber attachment to toner ink particles reduces flotation efficiency (9,10). Study of pulper samples indicated this fiber remained attached to a substantial fraction of toner ink particles in laboratory tests, pulping in two pilot plants, and in two commercial mills (9). The high shear environment of the ASH flotation cell could also promote additional detachment of hydrophilic fibers from toner particles. The resulting increased toner particle hydrophobicity leads to increased ink separation efficiency.

An earlier report described the results of pilot plant deinking of a PS-40 grade furnish containing 60-80% toner-printed paper (11). After forward cleaning, some of the few residual ink particles present exhibited elongated shapes (Fig. 2). Energy dispersive X-ray analysis indicated these elongated ink particles contain high levels of iron. Magnetite is a common toner ingredient but is not present in conventional inks. Therefore, we concluded these ink particles were formed largely from toner inks. Borchardt, et al. (11) suggested that ink particle fragmentation could have occurred in the relatively high shear environment of a forward cleaner. Some of the deinking agents used in this WTC study (11) can reduce toner glass transition temperature from about 160°F to about 104°F. Pulp slurry temperature was 70°-80°F which is significantly below either of these glass transition temperatures. The relationship of process temperature to glass transition temperature suggested that elongation of

Table 1. Specific Capacity of Different Flotation Cells.

Cell Type	Capacity (gal per min per ft^3)
Mechanical cells	1 - 5
Flotation column	1 - 5
ASH cell	200-400

FIGURE 2: **One of the few ink particles left after forward cleaning in a Western Michigan Univ. pilot plant deinking test using PS-40 grade furnish and SDA-43. Taken from reference 10. For another example of this type of particle geometry, see Fig. 12 in Ref. 10.**



softened toner particles in forward cleaners was unlikely. However, fragmentation of hard, brittle toner particles in the high shear environment was a reasonable concern. Borchardt, et al. (11) were concerned about toner ink behavior in the high shear environment of the forward cleaner and raised the issue of whether toner ink particle elongation or fragmentation could occur in the high shear environment of the ASH flotation cell. Either effect could have an adverse effect on deinked pulp properties. Excessive toner fragmentation could result in reduced pulp brightness (12). The long, thin shape of elongated ink particles could reduce ink removal efficiency in forward cleaners.

EXPERIMENTAL SECTION

Unless otherwise noted, pulping and deinking experiments were performed at the University of Utah. Microscopy studies were performed at the Shell Chemical Company Westhollow Research Center (WTC). Toners based on a styrene - acrylate copolymer were used in both the Utah and WTC experiments. These toners have a glass transition temperature T_g of about 160°F.

Pulping

Toner printed paper (1 kg), sodium tripolyphosphate (5g), sodium hydroxide (5g), and hot 80°-85°C, 176°-185°F) water (about 5 liters) was pulped for 5 minutes. Pulp consistency was thus about 16.6%. Pulping temperature was above the glass transition temperature of commonly used toners. The pulp was further dispersed in a high-speed blender for 30 seconds. It was then diluted to 1% consistency using room temperature water.

A suitable amount of deinking agent, 10 kgs per ton of dry furnish, was added to the pulp. This deinking agent was a mixture of one part frother, methyl-isobutyl carbinol, to 100 parts collector. The collector was a kerosene emulsion formed by mixing one part by weight of nonionic surfactant with 50 parts water and 50 parts kerosene. Total amount of deinking agent (frother + collector) added was 0.11% by weight relative to dry furnish.

Flotation

Air-sparged hydrocyclone flotation was carried out with a 2-inch ASH system. Handsheets were prepared from the pulp feed, flotation rejects (the froth or overflow) and the flotation accepts (the underflow). A Buchner funnel procedure was used to prepare these sheets.

Additional Experiments

Additional pulping and deinking experiments were performed at WTC. Test procedures are described in reference 10. A Denver Equipment Company Flotation Machine, not an ASH flotation cell, was used in these experiments. The deinking agents used were proprietary formulations sold under the tradename NONATELL® deinking surfactants. Since the primary ingredients of these deinking formulations were prepared from petrochemical feedstocks, they are referred to by the generic acronym, SDA, synthetic deinking agents.

Microscopy analyses were performed using procedures described in ref. 10.

RESULTS

Most of the ink particles studied using energy dispersive X-ray analysis were iron-rich verifying that these were toner particles. Some of the toner ink particles on handsheets made immediately after pulping have layered structures. Similar ink particles are seen in the flotation accepts and rejects (Fig. 3). Very few ink particles are present on the flotation accepts handsheets. Therefore, it is most unlikely that the Fig. 3 image represents residual toner particles that happened to deposit on top of each other during sheetmaking. It appears that the ink particles are softened during pulping, perhaps

FIGURE 3: **Layered structure of agglomerated toner ink particles. Individual two-dimensional toner flakes are partially fused together and can still be distinguished.**

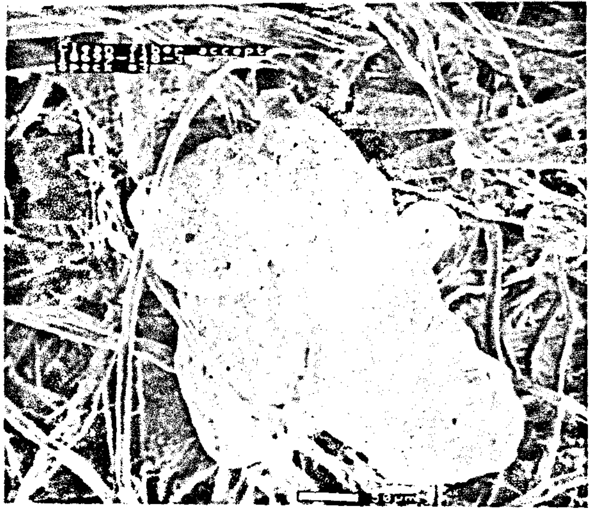
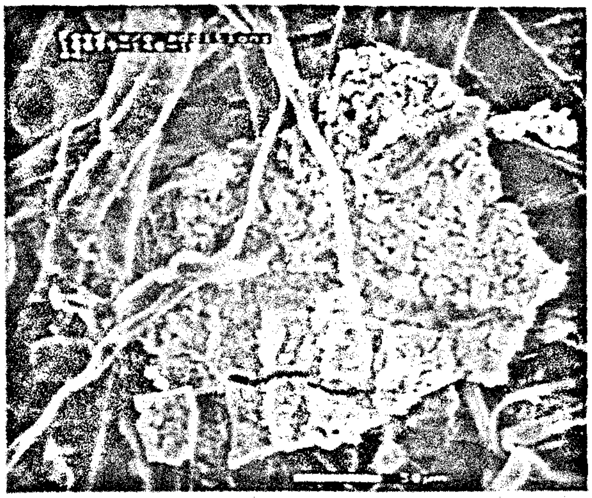


FIGURE 4: **Unusual toner ink particle after WTC pulping at 200°F in the absence of surfactant. The ink particle structure is probably due to the deposition of two ink particles on top of each other during sheetmaking.**

FIGURE 5: **Toner ink particle after pulping.**



by the oil phase of the emulsified deinking agent. The softened particles adhere to each other.

Somewhat different results were noted in WTC experiments performed at 200°F in the absence of any added surfactant (13). Despite pulping at temperatures considerably greater than toner softening points, microscopy analyses provided little evidence of ink particle aggregation or the formation of three-dimensional toner particles. In the Utah experiments, some cases of overlapping toner particles were noted after pulping (Fig. 4). However, these were absent in the flotation accepts which contained relatively few ink particles. This absence suggested that the overlapping ink particles imaged in Fig. 4 were due to particles being deposited on top of each other after sheetmaking. After flotation, when the statistical chances of this overlapping were slight due to removal of most of the dispersed ink, no evidence of overlapping ink particles were noted. The remaining few ink particles were quite flat.

After pulping, the University of Utah deinking tests produced relatively flat toner ink particles. All the ink particles imaged in the ESEM appeared flat and plate-like rather than spherical. (This was true for the flotation accepts and rejects as well as the pulper samples.) Confocal laser scanning microscopy studies confirmed the ESEM observations (14). (This microscopy technique and its application to the analysis of ink particles after pulping used office paper is discussed in ref. 11.)

The ink particle imaged in Fig. 5 is representative. On the lower portion of the image are two small ink particles that appear to have broken off from the main ink particle during sheetmaking. The main ink particle is also marked by a long horizontal groove. These grooves were observed in many of the ESEM-imaged ink particles. Similar grooves observed in ink particles repulped in the presence of SDA surfactants have been shown to be due to cellulose fibers detached from the ink (10).

Residual ink particles in the flotation accepts (underflow) not fused to other particles appear relatively thin and brittle (Figs. 6 and 7). Ink particles exhibiting cracks were quite common. Cracks commonly appear to extend completely through these ink particles. This can be seen more clearly in the enlarged ESEM image (Fig. 8). The upper left of the Fig. 7 ink particle image indicates that the large crack depicted in Fig. 8 does not extend completely across the ink particle. However, other pieces of the ink particle appear to have become completely de-

FIGURE 6: **Residual toner ink particle in the flotation accepts.**

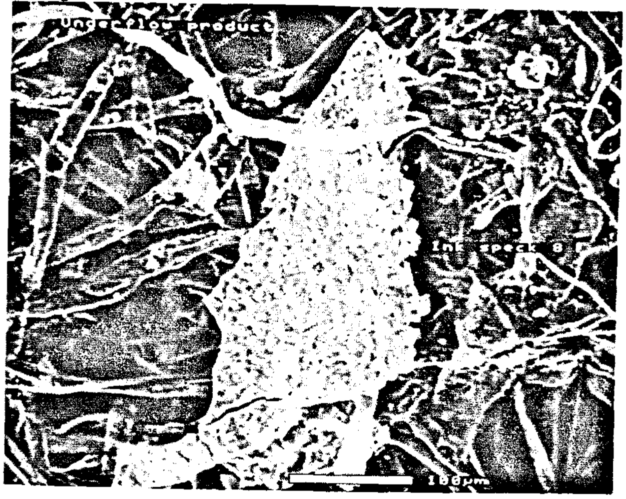


FIGURE 7: **Highly fragmented residual toner ink particle in the flotation accepts.**

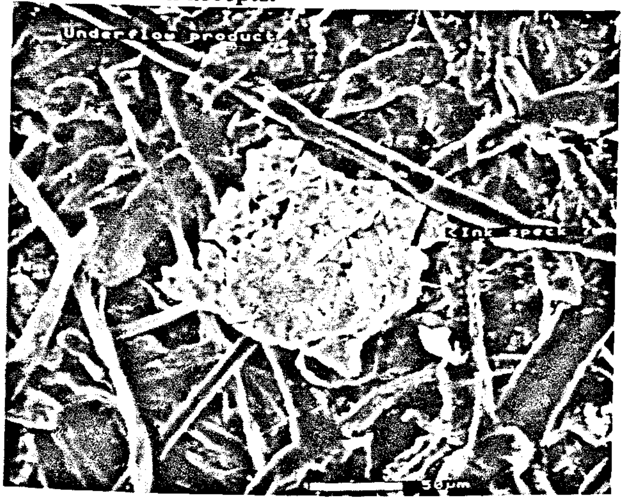


FIGURE 8: **Enlargement of the upper-left of the Figure 7 toner ink particle. Arrows indicate the fracture between the primary portion of the ink particle and a partially detached section.**

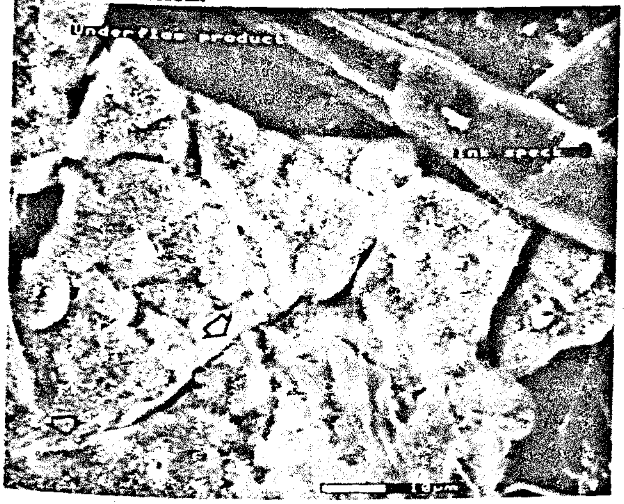
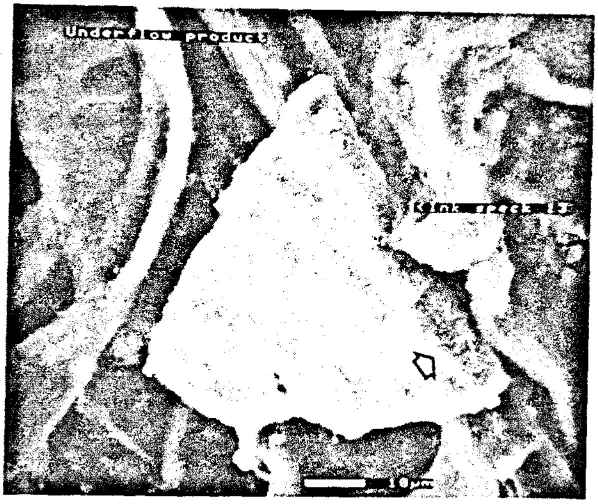


FIGURE 9: **Toner ink particle in the flotation rejects. This particle appears flat and flake-like. The arrow indicates a sharp edge along which part of the ink particle probably broke off.**



tached. Complete detachment may be due to the ink particle fracturing along previously formed cracks due to the impact of hitting paper fibers during sheetmaking.

Many of the ink particles in the flotation rejects (overflow) are also relatively flat (Fig. 9). The Fig. 8 image suggests these ink particles are brittle and easily broken. The lower ink particle appears to have broken off from the upper one. The two ink particles appear to fit together like matching pieces of a puzzle.

DISCUSSION

The furnish used in this study was prepared from sized stock and contains starch. So, despite the large amount of kerosene present in the deinking agent, it is unlikely that the liquid bridge agglomeration mechanism proposed by Snyder and Berg (15) is operative. [The presence of starches appeared to interfere with toner particle agglomeration (15).] An absence of liquid bridge agglomeration is consistent with the relatively flat toner ink particles produced after pulping in the present study.

Fig. 3 is an image of ink particles that have partially fused together. The high pulping temperature, 176°F, was greater than the nominal softening point of commonly used toners (16). Despite this high pulping temperature, softening was insufficient for the particles to fuse completely together as observed previously in WTC experiments using proprietary surfactants (10).

The relatively flat toner ink particle geometry observed in Figs. 5-7 and 9 suggest that, despite some toner ink particle softening, fragments of printed characters are detached from fibers and dispersed as flat flakes. In the absence of deinking agent, toner particle fragments can be quite small. The ink particle fragment in the lower left of Fig. 5 is approximately 20-25 microns in the longest ink particle dimension. The dispersed ink particles are insufficently softened to meld into each other to form highly three-dimensional objects when they collide. Rather, they seem to adhere to each other sufficiently to form a stacked structure reminiscent of a stack of kaolinite platelets or a stack of poker chips. These particles do have some three-dimensional character (Fig. 3). However, relative to their longest particle dimension, they remain relatively flat. Thus, the behavior of the frother/collector deinking agent used in the present study is significantly different than that of the SDA chemicals used in our earlier toner deinking studies (11). In these earlier studies, the highly three-dimensional toner and mixed office paper ink particle geometry after pulping were spherical, brick, and multi-lobed in shape (11).

All these toner ink particles are relatively small (17) compared to the toner ink particles produced in WTC deinking experiments using proprietary surfactants (11 and references cited therein). This may be due to their brittle nature (as indicated by the cracks in many ink particles) facilitating their fragmentation into smaller particles. Ink particle fragmentation could reduce the number of visible residual toner particles and thus improve deinked sheet appearance. However, the formation of an excessive number of microscopic ink particles could reduce deinked pulp brightness (12) causing increased bleaching agent consumption to attain a target brightness value. The appearance of some ink particles indicates ink particle softening occurred in the pulper (Fig. 2). However, the ink particles do not appear to be elongated by the high shear conditions associated with the ASH flotation cell.

The brittle nature of the toner ink particles observed in this study suggests that fragmentation of visible ink particles to form microscopic ink particles could be occurring. The small particles broken off from the main ink particles imaged in Figs. 5 and 7 (see also Fig. 8) support this hypothesis. Effective residual ink concentration (ERIC) and brightness studies could provide firm evidence to confirm or deny this hypothesis. So could image analysis using an instrument capable of detecting ink particles less than 50 microns in size.

Pulper chemistry in a commercial mill using ASH flotation could prevent extensive ink particle fragmentation into microscopic particles during the high shear conditions of pulping and flotation. If it does not, additional flotation or a washing step may be needed to remove microscopic ink particles and attain required deinked pulp brightness levels.

Other workers have noted that, after flotation deinking, there was no correlation of residual toner ink weight and ink particle area on deinked sheets (18). This is consistent with the presence of partially fused, flat ink particles observed in the present research. A "stack" of flat ink particles would be relatively heavy but occupy little more sheet area than a single ink particle.

CONCLUSIONS

1. Microscopy indicates ink particles in both the flotation accepts and rejects of the University of Utah deinking tests are relatively flat. Many of the ink particles appear to be brittle and easily broken into smaller ink particles.

2. Some ink particle softening has occurred as indicated by partial fusion of ink particles. Despite this softening, ESEM images suggest the ink particles are not elongated by the high shear conditions associated with the gas sparged cyclone flotation cell.

3. The frother/collector deinking agent appears to promote detachment of flat fragments of toner-printed characters from the fibers.

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